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(54) Title: METHOD FOR PRODUCING ETHANOLAMIDE ALKOXYLATE

(57) Abstract

Ethanolamide ethoxylate of the general formula $R^1CONHC_2H_4O(A)_xH$ wherein R^1 is a hydrocarbon group having 1-29 carbon atoms, A is an alkyleneoxy group derived from an alkylene oxide having 2-4 carbon atoms, and x is 2-30, is produced by reacting a compound of the general formula $R^1CONHC_2H_4OH$ wherein R^1 and n have the meanings stated above, with an alkylene oxide having 2-4 carbon atoms in the presence of a tertiary amine lacking protons that react with alkylene oxide, or an alkylene-oxide-quaternised derivative thereof at a temperature ranging from room temperature to 120 °C. This gives high yields of the ethoxylate, which has low contents of undesired secondary compounds. The ethoxylate is conveniently used in detergent compositions.

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METHOD FOR PRODUCING ETHANOLAMIDE ALKOXYLATE

The present invention relates to a method for producing high yields of ethanolamide alkoxylate with low contents of undesired by-products.

It is a well-known fact, disclosed e.g. in an article by H. Grossmann in Fette-Seifen-Anstrichmittel, No. 1, 74 (1972), pp 58-63, that non-ionic surface-active compounds can be produced by ethoxylation of fatty acid monoethanolamides in the presence of an alkaline catalyst at a temperature of 150-180°C. NaOH, KOH, $NaOCH_3$ and $KOCH_3$ have been used as catalyst. If a fatty acid monoethanolamide is reacted with 5 moles of ethylene oxide per mole of amide, this results, according to the article, in a reaction mixture of the following approximate composition:

I	Fatty acid amide ethoxylate	$RCONH(CH_2CH_2O)_x H$	80%
II	Ester amine ethoxylate	$RCOOCH_2CH_2N(CH_2CH_2O)_y H, (CH_2CH_2O)_z H$	6%
III	Nitrilotripolyglycol ether	$N(CH_2CH_2O)_r H, (CH_2CH_2O)_s H, (CH_2CH_2O)_t H$	8%
IV	Polyglycol ether	$HO(CH_2CH_2O)_u H$	2%
V	Fatty acid polyglycol ester	$RCOO(CH_2CH_2O)_v H$	4%

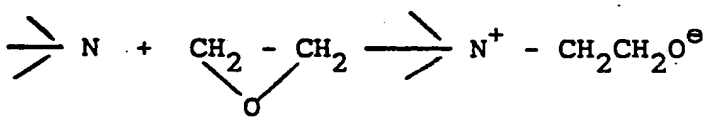
Being cationic, especially the by-products II and III are undesirable. Despite the fact that ethoxylated fatty acid monoethanolamides have been commercially available for more than 30 years, they still constitute but a small part of the total amount of non-ionic surface-active agents. This should mainly be attributed to the fact that it has only been possible to produce impure products as above,

unless one resorted to costly processing methods. Thus, there is a manifest need of carboxylic acid ethanolamide ethoxylate in high yields and with low contents of by-products.

The present invention relates to a new method for alkoxylating monoethanolamides, thereby obtaining compounds of type I in a yield of at least 95%, at the same time as the undesired compounds of types II and III are present in contents less than 1% by weight. According to the invention, ethanolamide alkoxylate of the general formula

$$R^{I}CONHC_2H_4O(A)_xH$$

wherein R^I is a hydrocarbon group having 1-29 carbon atoms, A is an alkyleneoxy group derived from an alkylene oxide having 2-4 carbon atoms, and x is 2-30, is produced by reacting the corresponding carboxylic acid monoethanolamide with an alkylene oxide having 2-4 carbon atoms in the presence of a tertiary amine lacking protons that react with alkylene oxide, or an alkylene-oxide-quaternised derivative of the tertiary amine at a temperature below 120°C, preferably 50-100°C. In the reaction conditions, the tertiary amine probably forms a zwitter compound with alkylene oxide in accordance with the reaction formula



whereupon the zwitterion compound reacts with the ethanolamide. The zwitterion compound is more basic than the amine from which it originates. Extensive tests have shown that, at temperatures exceeding 120°, other reaction mechanisms set in, which suppress the formation of the desired compounds. The suitable reaction temperature

according to the invention ranges from room temperature to 120°C, preferably 50-100°C, most preferred 70-80°C.

As mentioned earlier, the tertiary amine must not contain any protons that react with alkylene oxide. The nitrogen groups usually have substituents that contain hydrocarbon groups, such as acyclic hydrocarbon groups, cycloaliphatic or aromatic groups, or form a cyclic group with a divalent hydrocarbon group. The substituents may also contain other atoms which do not react with alkylene oxide, such as oxygen atoms in ether groups. Suitable tertiary amine compounds include trimethylamine, triethylamine, tributylamine, dimethyloctylamine, tetramethylethylenediamine, dimethyl coconut amine, tristearyl amine, and cyclic amines, such as dimethyl piperazine and diazabicyclooctane (Dabco). The preferred amine catalysts contain at least one substituent that consists of an alkyl group having 1-4 carbon atoms.

The amount of catalyst suitably is less than 15 mole% of the amount of ethanolamide. Higher contents of the catalyst do not increase the reaction rate. For practical reasons, the catalyst content should preferably be 5-8 mole%.

The carboxylic acid ethanolamide can actually be based on all types of monocarboxylic acids. Usually, the carboxylic acids contain 2-30 carbon atoms, preferably 8-20 carbon atoms. They may further be either synthetically produced or naturally derived.

In the alkoxylation, ethylene oxide, propylene oxide or butylene oxide can be added in one or more steps. If desired, several different alkylene oxides can be added in the same molecule, e.g. by random addition or stepwise addition of blocks of specific alkylene oxides, or by using both principles at the same time.

The ethanolamide alkoxylates can be used in a number of different detergent compositions, e.g. such compositions as are used for cleaning textiles and hard surfaces.

The present invention will now be further illustrated with the aid of the following Examples.

Example 1

Rape fatty acid monoethanolamide in an amount of 450 g (1.36 mole) was melted and batched in an ethoxylation reactor. Then, the reactor was treated with nitrogen gas, and 3.5 g of trimethylamine was batched as catalyst. The reactor temperature was raised to 75°C, and 244 g (5.44 mole) of ethylene oxide was fed to the reactor under intense cooling. The temperature was maintained at 75-80°C. After 20 min. when all the ethoxylene oxide had been batched, the temperature was raised to 80°C for 20 min. The resulting reaction mixture was vacuum-treated in the reactor, so that essentially all the catalyst was stripped, whereupon ethanol/water was added to strip the remaining amine and formed dioxane. The resulting reaction product was a bright yellow liquid having a cloud point of 81°C in an aqueous solution containing 25% by weight of butyl diethylene glycol. Potentiometric titration with 0.1 M HCl showed that the undesired products II and III amounted to about 0.4% by weight.

Example 2

Here, 560 g of linseed oil fatty acid monoethanolamide was batched in an ethoxylation reactor together with 13.18 g of the catalyst triethylamine after careful nitrogen-gas treatment. The reactor was heated to 80°C, and 173 g of ethylene oxide was supplied. The reactor temperature was maintained at 80°C. After 5.5 h, the reactor was evacuated and the triethylamine removed under vacuum. Potentiometric titration showed that the content of the undesired compounds II and III did not exceed about 0.5% by weight.

Example 3

Coconut fatty acid monoethanolamide in an amount of 890 g (3.34 mole) was batched in a reactor together with 78.7 g of dimethyloctylamine after careful nitrogen-gas treatment of the reactor. After a temperature increase to 80°C, 885 g of ethylene oxide was added for 1 h under intense cooling. After another 15 min. at 80°C, the reaction was interrupted, and the reaction mixture was treated with KH_2PO_4 and filtered in order to remove dimethyloctylamine. After filtering, potentiometric titration with 0.1 M HCl was unable to indicate the presence of any tertiary amine. The resulting reaction product had a cloud point of 58°C in an aqueous solution containing 10% by weight of NaCl.

Example 4

Tall oil fatty acid monoethanolamide in an amount of 640 g (1.9 mole) and 5.7 g of dimethyl piperazine were batched in a reactor which previously had been treated with nitrogen gas. Then, the reactor was heated to 70°C, and 251 g (5.7 mole) of ethylene oxide was batched at 70°C. The resulting reaction mixture was treated with acid ion exchanger in order to remove the catalyst. The resulting end product had extremely low contents of the tertiary nitrogen compound and further had a cloud point of 5°C in water and 96°C in water containing 25% by weight of butyl diethylene glycol.

Example 5

In the manner described above, 365 g (8,28 mole) of ethylene oxide was added to tall oil fatty acid monoethanolamide (1.9 mole) at 70°C. Tetramethylethylenediamine in an amount of 0.02 mole was used as catalyst, and was removed after the completed reaction by filtering with KH_2PO_4. The resulting end product had a cloud point of 27°C in water containing 10% NaCl. Gas chromatography

showed that compounds of type I were obtained in a yield of at least 98%.

CLAIMS

1. Method for producing ethanolamide alkoxylate of the general formula

$$R^{I}CONHC_2H_4O(A)_xH$$

wherein R^I is a hydrocarbon group having 1-29 carbon atoms, A is an alkyleneoxy group derived from an alkylene oxide having 2-4 carbon atoms, and x is 2-30, 2-30 moles of alkylene oxide having 2-4 carbon atoms being added to a compound of the formula

$$R^{I}CONHC_2H_4OH$$

wherein R^I and n have the meanings stated above, c h a r a c t e r i s e d in that the alkylene oxide is added in the presence of a tertiary amine lacking protons that react with alkylene oxide, or an alkylene-oxide-quaternised derivative of the tertiary amine at a temperature ranging from room temperature to 120°C.

2. The method of claim 1, c h a r a c t e r i s e d in that the addition is carried out at a temperature of 50-100°C.

3. The method of claim 1 or 2, c h a r a c t e r i s e d in that the tertiary amine is a trialkyl amine, at least one of the alkyl groups having 1-4 carbon atoms.

4. The method of claim 1 or 2, c h a r a c t e r i s e d in that the catalyst is a tetraalkylene diamine.

5. The method of claim 1 or 2, c h a r a c t e r i s e d in that the catalyst is a cyclic tertiary amine compound.

6. The method of any one of claims 1-6, c h a r a c t e r i s e d in that the tertiary amine or the alkylene-oxide-quaternised derivative thereof is present

in an amount less than 15 mole%, preferably 5-8 mole%, as based on the amount of ethanolamide.

7. Use of ethanolamide alkoxylate as set forth in claim 1, in detergent compositions.

INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 91/00752

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 07 C 231/12

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 07 C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in Fields Searched[8]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	Chemical Abstracts, volume 92, no. 1, 7 January 1980, (Columbus, Ohio, US), see page 573, abstract 6095f, & PO, A, 102560 (Fatty acid ethanolamides) 1979 --	1-7
A	DE, A, 2365751 (CIBA-GEIGY AG) 10 June 1976, see the whole document --	1-7
A	US, A, 4670591 (ALFRED OFTRING ET AL) 2 June 1987, see the whole document --	1-7

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
24th February 1992	1992 -02- 27
International Searching Authority	**Signature of Authorized Officer**
SWEDISH PATENT OFFICE	Solveig Gustavsson Solveig Gustavsson

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/SE 91/00752

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